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**(54) PROCESS FOR THE PREPARATION OF FLUORINATED OLEFIN**

**VERFAHREN ZUR HERSTELLUNG FLUORIERTER OLEFINE**

**PROCEDE DE PREPARATION D'OLEFINE FLUOREE**

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## Description

[0001] This invention relates to a process for preparing a fluorinated olefin having a carbon-carbon double bond, the carbon atoms of which have a fluorine atom.

[0002] Fluorinated olefins having a carbon-carbon double bond, the carbon atoms of which have a fluorine atom, are used as intermediate materials for fluorinated paraffins used as chlorofluorocarbon alternatives, and monomers for fluorinated polymers, and are produced in a large scale.

[0003] Heretofore, these fluorinated olefins have been produced by reacting an olefin compound having a carbon-carbon double bond, the carbon atoms of which have a chlorine atom, with an alkali metal fluoride. For example, 1,2,3,3,4,4,5,5-octafluorocyclopentene is produced by reacting 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene with potassium fluoride [U.S. Patent No. 3,024,290, *ibid.* 3,567,788, and J. Org. Chem., 28, 112 (1963)]. However, the yield of the intended product is insufficient for the production thereof in a commercial scale, and thus, enhancement of the yield is desired.

[0004] In view of the foregoing, the object of the invention is to provide an improved process for preparing a fluorinated olefin having a carbon-carbon double bond, the carbon atoms of which have a fluorine atom, by reacting a halogenated olefin having at least one carbon-carbon double bond, a carbon atom or the carbon atoms of which have a chlorine atom, and having the carbon atom or atoms with a single bond having no halogen atom other than a fluorine atom in the molecule, with an alkali metal fluoride, whereby the target fluorinated olefin is produced in an enhanced yield.

[0005] Thus, in accordance with the present invention, there is provided a process for preparing a fluorinated olefin represented by the following general formula (3)



wherein  $R^5$  and  $R^6$  independently represent an alkyl or fluoroalkyl group or a fluorine atom, or  $R^5$  and  $R^6$  are bonded together to form an alkylene or fluoroalkylene group by reacting a halogenated olefin represented by the following general formula (1):



wherein  $R^1$  and  $R^2$  independently represent an alkyl group, a fluoroalkyl group or a fluorine atom, or  $R^1$  and  $R^2$  may be bonded together to form an alkylene group or a fluoroalkylene group, with an alkali metal fluoride, characterized in that said reaction of the halogenated olefin with the alkali metal fluoride is conducted in the presence of an organic halogen-containing compound

represented by the following general formula (2):



wherein  $X^1$  and  $X^2$  represent a halogen atom, and  $R^3$  and  $R^4$  independently represent an alkyl group, a haloalkyl group or a halogen atom, or  $R^3$  and  $R^4$  are bonded together to form a haloalkylene group, and either  $R^3$  or  $R^4$  has a halogen atom other than fluorine atom which is capable of reacting with the alkali metal fluoride to give the intended halogenated olefin of formula (3).

#### Halogenated Olefin

[0006] The number of carbon atoms in the halogenated olefin (1) is not particularly limited, but is usually in the range of from 2 to 30, preferably from 3 to 20 and more preferably from 4 to 10.

[0007] When  $R^1$  and  $R^2$  in formula (1) are fluoroalkyl groups or bonded together to form a fluoroalkylene group, the reaction takes place rather rapidly and therefore these groups are preferable. The number of carbon atoms in the alkyl, fluoroalkyl, alkylene and fluoroalkylene groups is not particularly limited, but is usually in the range of from 1 to 20, preferably from 2 to 10 and more preferably from 2 to 8.

[0008] As specific examples of the alkyl group, there can be mentioned methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, n-amyl, isoamyl, t-amyl, n-hexyl and n-octyl groups.

[0009] As specific examples of the fluoroalkyl group, there can be mentioned fluoromethyl, difluoromethyl, trifluoromethyl, 1,2,2-trifluoroethyl, 1,1,2,2-tetrafluoroethyl, 1,1,1,2,2-pentafluoroethyl, 1,2,2,3,3-pentafluoropropyl, 1,1,2,2,3,3-hexafluoropropyl and 1,1,1,2,2,3,3-heptafluoropropyl groups. Of these, perfluoroalkyl groups such as trifluoromethyl, 1,1,1,2,2-pentafluoroethyl and 1,1,1,2,2,3,3-heptafluoropropyl groups are preferable.

[0010] As specific examples of the alkylene group, there can be mentioned propylene, isopropylene, butylene, amylene and hexylene groups. Of these, propylene, butylene and amylene groups are preferable. A propylene group is most preferable.

[0011] As specific examples of the fluoroalkylene group, there can be mentioned 1,1,2,2-tetrafluoropropylene, 1,1,2,2,3-pentafluoropropylene, 1,1,2,2,3,3-hexafluoropropylene, 1,1,2,2,3,3,4-heptafluorobutylene and 1,1,2,2,3,3,4,4-octafluorobutylene. Of these, perfluoroalkylene groups such as 1,1,2,2,3,3-hexafluoropropylene and 1,1,2,2,3,3,4,4-octafluorobutylene are preferable. 1,1,2,2,3,3-Hexafluoropropylene is most preferable.

[0012] As specific examples of the halogenated ole-

fin, there can be mentioned straight chain halogenated olefin compounds such as 2,3-dichloro-1,1,1,4-tetrafluoro-2-butene, 2,3-dichloro-1,1,1,4,4-pentafluoro-2-butene, 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene, 1,2-dichloro-1,3,3,4-tetrafluoro-1-butene, 1,2-dichloro-1,3,3,4,4-pentafluoro-1-butene, 1,2-dichloro-1,3,3,4,4,4-hexafluoro-1-butene, 1,2-dichloro-1,3,3,4,4,5-hexafluoro-1-pentene, 1,2-dichloro-1,3,3,4,4,5,5-heptafluoro-1-pentene, 1,2-dichloro-1,3,3,4,4,5,5,5-octafluoro-1-pentene, 2,3-dichloro-1,1,1,4,4,5-hexafluoro-2-pentene, 2,3-dichloro-1,1,1,4,4,5,5-heptafluoro-2-pentene and 2,3-dichloro-1,1,1,4,4,5,5,5-octafluoro-2-pentene; and alicyclic halogenated olefin compounds such as 1,2-dichloro-3,3,4,4-tetrafluorocyclopentene, 1,2-dichloro-3,3,4,4,5-pentafluorocyclopentene, 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene, 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclohexene, 1,2-dichloro-3,3,4,4,5,5,6-heptafluorocyclohexene and 1,2-dichloro-3,3,4,4,5,5,6,6-octafluorocyclohexene.

[0013] These halogenated olefins may be used either alone or as a combination of at least two thereof.

#### Organic Halogen-Containing Compound

[0014] The organic halogen-containing compound used in the present invention is, in view of the separation and purification of the intended fluorinated olefin, an organic halogen-containing compound capable of reacting with an alkali metal fluoride to give the intended halogenated olefin.

[0015]  $X^1$  and  $X^2$  in the formula (2) represent a halogen atom which specifically includes fluorine, chlorine, bromine and iodine atoms. Of these, fluorine and chlorine atoms are preferable. A chlorine atom is most preferable.

[0016]  $R^3$  and  $R^4$  in the formula (2) independently represent an alkyl group, a haloalkyl group or a halogen atom, or  $R^3$  and  $R^4$  are bonded together to form a haloalkylene group, and either  $R^3$  or  $R^4$  has a halogen atom other than fluorine atom. Of these, haloalkyl and haloalkylene groups are preferable. The number of carbon atoms in the alkyl, haloalkyl, and haloalkylene groups is not particularly limited, but is usually in the range of from 1 to 20, preferably from 2 to 10 and more preferably from 2 to 8.

[0017] As specific examples of the alkyl groups, there can be mentioned those which are recited for  $R^1$  and  $R^2$  in the formula (1).

[0018] The halogen in the haloalkyl and haloalkylene groups is characterized as representing at least one halogen atom other than a fluorine atom. Such halogen atom includes, for example, chlorine, bromine and iodine atoms. These halogen atoms other than a fluorine atom may be used either alone or as a combination of at least two thereof. These halogen atoms may be used in combination with a fluorine atom. Of these, a combination of

a chlorine atom with a fluorine atom is preferable.

[0019] As specific examples of the haloalkyl group, there can be mentioned chlorofluoromethyl, chlorodifluoromethyl, dichlorofluoromethyl, 1-chloro-2,2-difluoroethyl, 1-chloro-1,2,2-trifluoroethyl, 1,1-dichloro-1,2,2-trifluoroethyl, 1-chloro-1,1,2,2-tetrafluoroethyl, 1-chloro-2,2,3,3-tetrafluoropropyl, 1-chloro-1,2,2,3,3-pentafluoropropyl, 1,1-dichloro-1,2,2,3,3-pentafluoropropyl and 1-chloro-1,1,2,2,3,3-hexafluoropropyl groups. Of these, chlorodifluoromethyl, dichlorofluoromethyl, 1,1-dichloro-1,2,2-trifluoroethyl, 1-chloro-1,1,2,2-tetrafluoroethyl, 1,1-dichloro-1,2,2,3,3-pentafluoropropyl and 1-chloro-1,1,2,2,3,3-hexafluoropropyl groups are preferable. A chlorodifluoromethyl group is especially preferable.

[0020] As specific examples of the haloalkylene group, there can be mentioned 1-chloro-1,2,2-trifluoropropylene, 1,3-dichloro-1,2,2-trifluoropropylene, 1-chloro-1,2,2,3-tetrafluoropropylene, 1,3-dichloro-1,2,2,3-tetrafluoropropylene, 1-chloro-1,2,2,3,3-pentafluoropropylene, 2-chloro-1,1,2,3,3-pentafluoropropylene, 2,2-dichloro-1,1,3,3-tetrafluoropropylene, 1,2-dichloro-1,2,3,3-tetrafluoropropylene, 2-chloro-1,1,2,3,3,4,4-heptafluorobutylene, 2,2-dichloro-1,1,3,3,4,4-hexafluorobutylene, 1-chloro-1,2,2,3,3-pentafluorobutylene, 1,4-dichloro-1,2,2,3,3-pentafluorobutylene, 1-chloro-1,2,2,3,3,4-hexafluorobutylene, 1,4-dichloro-1,2,2,3,3,4-hexafluorobutylene and 1-chloro-1,2,2,3,3,4,4-heptafluorobutylene groups. Of these, 1,3-dichloro-1,2,2,3-tetrafluoropropylene, 2,2-dichloro-1,1,3,3-tetrafluoropropylene, 1-chloro-1,2,2,3,3-pentafluoropropylene, 2-chloro-1,2,2,3,3-pentafluoropropylene, 1,4-dichloro-1,2,2,3,3,4-hexafluorobutylene and 1-chloro-1,2,2,3,3,4,4-heptafluorobutylene groups are preferable. 1,3-Dichloro-1,2,2,3-tetrafluoropropylene, 2,2-dichloro-1,1,3,3-tetrafluoropropylene, 1-chloro-1,2,2,3,3-pentafluoropropylene and 2-chloro-1,2,2,3,3-pentafluoropropylene groups are especially preferable.

[0021] These organic halogen-containing compounds may be used either alone or as a combination of at least two thereof. The amount of the halogen-containing compounds can be suitably chosen depending upon the particular reaction conditions and the content of halogen atoms in the molecule, and is usually in the range of from 1 to 200 parts by weight, preferably from 10 to 100 parts by weight and more preferably from 20 to 80 parts by weight, based on 100 parts by weight of the above-mentioned halogenated olefin. If the amount of the organic halogen-containing compound is too small, the yield of the target compound is not enhanced to the desired extent. By contrast, if the amount of the organic halogen-containing compound is too large, the amount of the alkali metal fluoride used is inevitably large which is economically disadvantageous.

### Preferable Usage of Halogenated Olefin and Organic Halogen-Containing Compound

[0022] In the present invention, the above-mentioned halogenated olefin is preferably supplied for the reaction as a mixture thereof with the above-mentioned organic halogen-containing compound. As a preferable example of the mixture, there can be mentioned a reaction product mixture prepared by reacting a perhalogenated conjugated diene and/or a perhalogenated olefin, which have been prepared by substituting the entire hydrogen atoms of conjugated diene by halogen atoms other than a fluorine atom, with hydrogen fluoride.

[0023] The perhalogenated conjugated diene, prepared by substituting the entire hydrogen atoms of a conjugated diene by halogen atoms other than a fluorine atom, is not particularly limited, but usually a perchloro-conjugated diene is used. A perchloro-conjugated diene is easily prepared by reacting a conjugated diene hydrocarbon with chlorine gas according to a process, for example, described in British Patent No. 1,070,891. As specific examples of the perchloro-conjugated diene, there can be mentioned aliphatic perchloro-conjugated dienes such as hexachloro-1,3-butadiene, octachloro-1,3-pentadiene, decachloro-1,3-hexadiene and tetradechchloro-1,3-octadiene; and alicyclic perchloro-conjugated dienes such as hexachlorocyclo-1,3-pentadiene, octachlorocyclo-1,3-hexadiene and dodecachlorocyclo-1,3-octadiene. Of these, hexachloro-1,3-butadiene and hexachlorocyclo-1,3-pentadiene are generally used. These perhalogenated conjugated dienes can be used either alone or as a combination of at least two thereof.

[0024] The perhalogenated olefin, prepared by substituting the entire hydrogen atoms by halogen atoms other than a fluorine atom, is not particularly limited, but usually perchloroolefins are used because these are readily available. Perchloroolefins are prepared by reacting the above-mentioned perchloro-conjugated diene further with chlorine gas in the presence of a catalyst such as aluminum trichloride according to a process, for example, described in J. Am. Chem. Soc., 71, 946 (1949). As specific examples of the perchloroolefin, there can be mentioned aliphatic perchloroolefins such as octachloro-1-butene, octachloro-2-butene, decachloro-1-pentene, decachloro-2-pentene, hexadecachloro-1-octene and hexadecachloro-2-octene; and alicyclic perchloroolefins such as octachlorocyclopentene, decachlorocyclohexene and tetradecachlorocyclooctene. Of these, octachloro-2-butene, decachloro-2-pentene, octachlorocyclopentene and decachlorocyclohexene are preferable. Octachlorocyclopentene is especially preferable. These perhalogenated olefins may be used either alone or as a combination of at least two thereof.

[0025] The reaction of the perhalogenated conjugated diene or perhalogenated olefin with hydrogen fluoride can be carried out by an ordinary procedure. Usu-

ally, hydrogen fluoride is used in an amount of at least 1 equivalent, preferably from 1 to 10 equivalent and more preferably from 1 to 5 equivalent, based on the halogen atoms in the raw material (i.e., perhalogenated conjugated diene or perhalogenated olefin); and the reaction is carried out in the presence of an antimony halide catalyst such as antimony pentachloride, antimony trifluoride dichloride and antimony pentafluoride in an amount of from 0.01 to 20 times by mole, preferably from 0.1 to 10 times by mole and more preferably 0.5 to 5 times by mole, based on the amount of the raw material. The reaction temperature employed is usually in the range of from 20 to 200°C, preferably from 60 to 160°C and more preferably 80 to 120°C. The reaction pressure employed is usually in the range of from 0.10-2.94 MPa (1 to 30 kg/cm<sup>2</sup>), preferably from 0.29-1.96 MPa (3 to 20 kg/cm<sup>2</sup>) and more preferably from 0.49-1.47 MPa (5 to 15 kg/cm<sup>2</sup>). The reaction time employed is usually in the range of from 0.5 to 48 hours and preferably 1 to 10 hours.

### Alkali Metal Fluoride

[0026] The alkali metal fluoride used in the present invention is not particularly limited provided that it is used in ordinary chemical reactions. The alkali metal fluoride includes, for example, lithium fluoride, sodium fluoride, potassium fluoride, cesium fluoride and rubidium fluoride. Of these, potassium fluoride, sodium fluoride and cesium fluoride are preferable.

[0027] The alkali metal fluoride may be used either alone or as a combination of at least two thereof. The amount of the alkali metal fluoride is usually in the range of from 1 to 3 equivalent weight, preferably from 1.1 to 2.0 equivalent weight and more preferably from 1.2 to 1.5 equivalent weight, based on the total amount of the halogen atoms, other than a fluorine atom, contained in the above-mentioned halogenated olefin and the above-mentioned organic halogen-containing compound. When the amount of the alkali metal fluoride is in this range, the target compound can be produced in a high yield and at a relatively low production cost.

### Fluorination Reaction

[0028] The fluorination reaction according to the process of the invention is usually carried out in an organic medium. The organic medium used is not particularly limited, but an aprotic polar solvent is preferably used. As specific examples of the polar solvent, there can be mentioned dimethylformamide, dimethylacetamide, N-methylpyrrolidone, N,N-dimethylimidazolidinone, dimethylsulfoxide and sulfolane.

[0029] The organic medium may be used either alone or as a mixture of at least two thereof. The amount of the organic medium is, in view of the yield of the target compound, usually in the range of from 100 to 1,000 parts by weight, preferably from 120 to 600 parts by

weight and more preferably from 150 to 300 parts by weight, based on 100 parts by weight of the alkali metal fluoride.

**[0030]** The fluorination reaction can be carried out by an ordinary procedure, and is usually carried out by heating the above-mentioned primary and secondary raw materials with stirring. The reaction temperature is usually in the range of from 50 to 250°C and preferably from 80 to 250°C, and the reaction pressure is not particularly limited and may be either a high pressure or a reduced pressure. The reaction time is suitably chosen depending upon the particular reaction conditions and is usually in the range of from 0.5 to 15 hours and preferably from 1 to 9 hours.

**[0031]** The fluorination reaction can be carried out either a batchwise or continuous manner. The fluorinated olefin, i.e., the reaction product has a boiling point lower than those of the halogenated olefin, i.e., substrate, and intermediates produced in the midway of fluorination, and therefore, the reaction is preferably conducted while the reaction product is taken off from a reactor equipped with a fractionating column at the top of the reactor.

**[0032]** In the fluorination reaction according to the invention, the entire amounts of the above-mentioned halogenated olefin and organic halogen-containing compound can be charged in a reactor at once before the initiation of reaction, but preferably at least part of the raw materials is supplied in the midway of reaction. The rate of supply is suitably chosen depending upon the particular rate of the reaction product flowing out from the reactor.

**[0033]** More specifically, it is advantageous from an industrial viewpoint that the fluorination reaction is conducted in an open system by using a reactor equipped with a rectification column, while the above-mentioned halogenated olefin and organic halogen-containing compound are supplied into an organic medium in which an alkali metal fluoride has been dispersed, and the reaction product is taken out. In this process, preferably only the target reaction product is concentrated and isolated with a good purity, and simultaneously, the raw materials and the reaction intermediates are returned back to the reactor as reflux without taking out from the reaction system to the outside.

**[0034]** Utilizing the fact that the fluoroolefin (target product) has a boiling point lower than those of the raw materials and the intermediate products, the raw materials are sequentially supplied to the reaction system comprising a reactor equipped with a rectification column, and simultaneously, the reaction product is taken out from the top of the rectification column. By adopting this procedure, the yield of the fluorinated olefin can be enhanced, and the amount of the reaction medium can be greatly reduced as compared with the conventional procedure. Further, the raw materials and the intermediate products are sequentially returned back to the reactor, and therefore, the amount of the alkali metal fluoride used can be greatly reduced even at a low reaction

temperature as compared with the conventional procedure.

**[0035]** The halogenated olefin and the organic halogen-containing compound can be supplied separately, but preferably these raw materials are supplied as a mixture thereof. The rate of supply is chosen depending upon the rate of flow-out of the product. When the supply of the raw materials is excessive, the residence time of the reaction product becomes inevitably long with the result of reduction of yield. The rate (mol/hr) of supply of the raw materials is usually not larger than three times, preferably from 0.1 to 2 times and more preferably from 0.5 to 1.5 times of the rate (mol/hr) of flow-out of the product.

**[0036]** The reaction product can be obtained by controlling the temperature at the top of the rectification column. The temperature at the top thereof can be set at a temperature approximately equal to the boiling point of the reaction product (which is determined depending upon the pressure) by appropriately setting the reflux ratio so as to conform to the capacity of the rectification column. The recovery of the target product can be carried out by a conventional procedure.

#### Fluorinated Olefin

**[0037]** As specific examples of R<sup>5</sup> and R<sup>6</sup> in the formula (3), there can be mentioned those which are hereinbefore recited for R<sup>1</sup> and R<sup>2</sup> in the formula (1).

**[0038]** As specific examples of the fluorinated olefin, there can be mentioned 1,1,2,3,3,3-hexafluoropropene, 1,1,2,3,3,4-hexafluoro-1-butene, 1,1,1,2,3,4-hexafluoro-2-butene, 1,1,2,3,3,4,4-heptafluoro-1-butene, 1,1,1,2,3,4,4-heptafluoro-2-butene, 1,1,2,3,3,4,4,4-octafluoro-1-butene, 1,1,1,2,3,4,4,4-octafluoro-2-butene, 1,1,2,3,3,4,4,5-octafluoro-1-pentene, 1,1,1,2,3,4,4,5-octafluoro-2-pentene, 1,1,2,3,3,4,4,5,5-nonafluoro-1-pentene, 1,1,1,2,3,4,4,5,5-nonafluoro-2-pentene, 1,1,2,3,3,4,4,5,5,5-decafluoro-1-pentene, 1,1,1,2,3,4,4,5,5,5-decafluoro-2-pentene, 1,2,3,3,4,4-hexafluorocyclopentene, 1,2,3,3,4,4,5-heptafluorocyclopentene, 1,2,3,3,4,4,5,5-octafluorocyclopentene, 1,2,3,3,4,4,5,5-octafluorocyclohexene, 1,2,3,3,4,4,5,5,6-nonafluorocyclohexene and 1,2,3,3,4,4,5,5,6,6-decafluorocyclohexene.

**[0039]** The invention will now be described in detail by the following working examples that by no means limit the scope of claim of the invention.

#### Production Example 1 [Preparation of Halogenated Olefin Mixture (I)]

**[0040]** A 7-liter stainless steel reactor equipped with a cooling reflux condenser and a pressure-keeping valve was charged with 950 g of antimony pentachloride and 330 g of hexachlorocyclopentadiene, and 100 g of chlorine gas at a pressure of 0.49 MPa (5 kg/cm<sup>2</sup>) at

80°C was introduced. The mixture was allowed to react for 2 hours. The unreacted residual chlorine gas was discharged, and 210 g of anhydrous hydrogen fluoride was introduced to allow the hydrogen fluoride to react at a temperature of 84°C and a pressure of 0.67 MPa (7 kg/cm<sup>2</sup>) while hydrogen chloride gas produced by a side-reaction was discharged through the pressure-keeping valve. After the generation of hydrogen chloride gas ceased, the pressure was reduced to the normal pressure and the residual hydrogen fluoride was removed, and then, the reaction was further conducted at 140°C for 5 hours. Simultaneously with the reaction, fractions with a boiling point of from 70 to 100°C were collected and neutralized with an aqueous sodium bicarbonate solution to give 280 g of a halogenated olefin mixture (I). GC-MS analysis of the mixture (I) revealed that it contained 61.7% by weight of 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene, 30.9% by weight of 1,2,3-trichloro-3,4,4,5,5-pentafluorocyclopentene, 7.1% by weight of 1,2,3,5-tetrachloro-3,4,4,5-tetrafluorocyclopentene and 0.3% by weight of 1,2,3,3,5-pentachloro-4,4,5-trifluorocyclopentene.

#### Production Example 2 [Preparation of Halogenated Olefin Mixture (II)]

**[0041]** The ingredients in the halogenated olefin mixture (I) were separated by fractionation. The thus-separated ingredients were mixed together to prepare a halogenated olefin mixture comprising 80% by weight of 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene, 10% by weight of 1,2,3-trichloro-3,4,4,5,5-pentafluorocyclopentene and 10% by weight of 1,2,3,5-tetrachloro-3,4,4,5-tetrafluorocyclopentene.

#### Example 1

**[0042]** A 200 ml four-necked flask equipped with a dropping funnel, a rectification column, a thermometer and a stirring device was charged under a nitrogen gas stream with 36.9 g (0.635 mol) of potassium fluoride and 75 ml of dimethylformamide. A cooling medium maintained at -10°C was circulated into a Dimroth condenser equipped at the top of the rectification column, and a trap for fraction was cooled to -70°C. 51.6 g of the halogenated olefin mixture (I) prepared in Production Example 1 was charged in the dropping funnel, and, when the inner temperature of the flask reached 135°C, the mixture (I) was continuously dropped over a period of 3 hours. When 1.5 hours elapsed from the commencement of reaction, the temperature at the top of the rectification column reached the boiling point of the reaction product (i.e., 27°C) and was stabilized, and, during the period spanning from this time when the temperature was stabilized to the time when the temperature at the top of column rose, the reaction product was intermittently drawn to give 40.4 g of 1,2,3,3,4,4,5,5-octafluorocyclopentene [purity: 99.9%, yield on the basis of the

total halogenated olefin mixture (I): 93.1%].

#### Comparative Example 1

**[0043]** Fluorination reaction was carried out by the same procedures as employed in Example 1 except that 50.2 g of 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentane was used instead of 51.6 g of the halogenated olefin mixture (I) with all other conditions remaining the same. 38.2 g of 1,2,3,3,4,4,5,5-octafluorocyclopentane was obtained [purity: 99.8%, yield on the basis of 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentane: 87.8%].

#### Example 2

**[0044]** Fluorination reaction was carried out by the same procedures as employed in Example 1 except that the halogenated olefin mixture (II) was used instead of the halogenated olefin mixture (I) with all other conditions remaining the same to give 1,2,3,3,4,4,5,5-octafluorocyclopentene [yield on the basis of the total halogenated olefin mixture (II): 92.0%, purity 99.7%].

#### Example 3

**[0045]** Fluorination reaction was carried out by the same procedures as employed in Example 1 except that 96.5 g (0.635 mol, 1.26 equivalent weight on the basis of chlorine atom) of cesium fluoride was used instead of potassium fluoride and 190 ml of dimethylformamide was used. All other conditions remained the same. 40.20 g (0.190 mol) of 1,2,3,3,4,4,5,5-octafluorocyclopentene [yield on the basis of the total halogenated mixture (I): 92.6%, purity: 99.80%] was obtained.

#### Example 4

**[0046]** A halogenated olefin mixture (III) was prepared from octachlorocyclopentene according to the procedure described in DE-A1 3,935,493. The obtained halogenated olefin mixture (III) contained 80% by weight of 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene and by-products similar to those recited in Example 1.

**[0047]** Fluorination reaction was conducted by the same procedures as employed in Example 1 except that the halogenated olefin mixture (III) was used instead of the halogenated olefin mixture (I) with all other conditions remaining the same to give 1,2,3,3,4,4,5,5-octafluorocyclopentene [yield on the basis of the total halogenated olefin mixture (III): 90.5%].

**[0048]** By the process for preparing a fluorinated olefin according to the present invention, a chlorine atom or atoms bound to a carbon atom or the carbon atoms of the carbon-carbon double bond can be substituted by a fluorine atom, and thus, a corresponding halogenated olefin with a high purity can be produced on a large scale and effectively, and in a high yield. Further, in the proc-

ess of the present invention, a reaction product mixture obtained by reacting a perchloro-conjugated diene or perchloro-olefin with hydrogen fluoride can be used as it is, without purification, as the substrate.

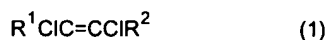
[0049] A fluorinated alkane can be produced on a large scale by further hydrogenating the fluorinated olefin prepared by the process of the present invention. The fluorinated olefin and the fluorinated alkane are useful as chlorofluorocarbon alternatives and intermediates therefor, and raw materials for medicines, pesticides, liquid crystals and polymers.

#### Claims

1. A process for producing a fluorinated olefin having a carbon-carbon double bond, represented by the following formula (3):



wherein  $R^5$  and  $R^6$  independently represent an alkyl or fluoroalkyl group or a fluorine atom, or  $R^5$  and  $R^6$  are bonded together to form an alkylene or fluoroalkylene group, by allowing a halogenated olefin, represented by the following general formula (1):



wherein  $R^1$  and  $R^2$  independently represent an alkyl group, a fluoroalkyl group or a fluorine atom, or  $R^1$  and  $R^2$  are bonded together to form an alkylene group or a fluoroalkylene group, to react with an alkali metal fluoride,

characterized in that said reaction of the halogenated olefin with the alkali metal fluoride is conducted in the presence of an organic halogen-containing compound represented by the following general formula (2):



wherein  $X^1$  and  $X^2$  represent a halogen atom, and  $R^3$  and  $R^4$  independently represent an alkyl group, a haloalkyl group or a halogen atom, or  $R^3$  and  $R^4$  are bonded together to form a haloalkylene group, and either  $R^3$  or  $R^4$  has a halogen atom other than a fluorine atom; said organic halogen-containing compound of the formula (2) being capable of reacting with the alkali metal fluoride to give the intended halogenated olefin of the formula (3).

2. The process according to claim 1, wherein the

amount of the organic halogen-containing compound is in the range of from 1 to 200 parts by weight based on 100 parts by weight of the halogenated olefin.

3. The process according to claim 1 or claim 2, wherein the halogenated olefin has 2 to 30 carbon atoms.
4. The process according to claim 3, wherein the alkyl, fluoroalkyl, alkylene and fluoroalkylkylene groups for  $R^1$  and  $R^2$  in the formula (1) have from 1 to 20 carbon atoms.
5. The process according to claim 3, wherein  $R^1$  and  $R^2$  in the formula (1) are a fluoroalkyl group or are bonded together to form a fluoroalkylene group.
6. The process according to any of claims 1 to 5, wherein the halogenated olefin is subjected to the reaction as a mixture thereof with the organic halogen-containing compound.
7. The process according to claim 6, wherein the mixture of the halogenated olefin with the organic halogen-containing compound is a reaction product mixture prepared by reacting at least one compound selected from perhalogenated conjugated dienes and perhalogenated olefins, which have been prepared by substituting the entire hydrogen atoms of conjugated dienes by halogen atoms other than a fluorine atom, with hydrogen fluoride.
8. The process according to any of claims 1 to 7, wherein the amount of the alkali metal fluoride is in the range of from 1 to 3 equivalent based on the amount of the total halogen atoms other than a fluorine atom contained in the sum of the halogenated olefin and the organic halogen-containing compound.
9. The process according to any of claims 1 to 8, wherein the alkali metal fluoride is lithium fluoride, sodium fluoride, potassium fluoride, cesium fluoride or rubidium fluoride.
10. The process according to any of claims 1 to 9, wherein the reaction is carried out in an organic medium.
11. The process according to claim 10, wherein the amount of the organic medium is in the range of from 100 to 1,000 parts by weight based on 100 parts by weight of the alkali metal fluoride.
12. The process according to claim 10 or claim 11, wherein the organic medium is an aprotic polar solvent.

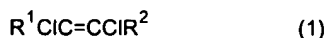
13. The process according to claim 12, wherein the aprotic polar solvent is dimethylformamide, dimethylacetamide, N-methylpyrrolidone, N,N-dimethylimidazolidinone, dimethylsulfoxide or sulfolane.
14. The process according to any of claims 1 to 13, wherein the reaction is carried out while the fluorinated olefin is drawn from a reactor which is equipped with a rectification column at the upper part of the reactor.
15. The process according to any of claims 1 to 14, wherein the reaction is carried out in an open system while the halogenated olefin and organic halogen-containing compound are supplied into an organic medium in which the alkali metal fluoride has been dispersed, and while the fluorinated olefin is taken out.

#### Patentansprüche

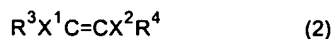
1. Verfahren zur Herstellung eines fluorierten Olefins mit einer Kohlenstoff-Kohlenstoff-Doppelbindung der folgenden Formel (3)



wobei  $R^5$  und  $R^6$  jeweils unabhängig voneinander einen Alkyl-, Fluoralkylrest oder ein Fluoratom darstellen oder  $R^5$  und  $R^6$  miteinander verbunden sind, um einen Alkyl- oder Fluoralkylenrest zu bilden, durch Umsetzen eines halogenierten Olefins der folgenden allgemeinen Formel (1)



wobei  $R^1$  und  $R^2$  jeweils unabhängig voneinander einen Alkyl-, Fluoralkylrest oder ein Fluoratom darstellen oder  $R^1$  und  $R^2$  miteinander verbunden sind, um einen Alkyl- oder Fluoralkylenrest zu bilden, mit einem Alkalimetallfluorid, **dadurch gekennzeichnet, dass** das Umsetzen des halogenierten Olefins mit dem Alkalimetallfluorid in Anwesenheit einer organischen, halogenhaltigen Verbindung der folgenden allgemeinen Formel (2)



wobei  $X^1$  und  $X^2$  ein Halogenatom und  $R^3$  und  $R^4$  jeweils unabhängig voneinander einen Alkyl-, Halogenalkylrest oder ein Halogenatom darstellen oder  $R^3$  und  $R^4$  miteinander verbunden sind, um ei-

nen Halogenalkylenrest zu bilden, und entweder  $R^3$  oder  $R^4$  ein von einem Fluoratom verschiedenes Halogenatom aufweist, durchgeführt wird, wobei die organische, halogenhaltige Verbindung der Formel (2) mit dem Alkalimetallfluorid reagieren kann, um das beabsichtigte Olefin der Formel (3) zu erhalten.

2. Verfahren gemäß Anspruch 1, wobei die Menge der organischen, halogenhaltigen Verbindung im Bereich von 1 bis 200 Gewichtsteilen bezogen auf 100 Gewichtsteile halogeniertem Olefin liegt.
3. Verfahren gemäß Anspruch 1 oder Anspruch 2, wobei das halogenierte Olefin 2 bis 30 Kohlenstoffatome aufweist.
4. Verfahren gemäß Anspruch 3, wobei die Alkyl-, Fluoralkyl-, Alkyl- und Fluoralkylenreste für  $R^1$  und  $R^2$  in der Formel (1) 1 bis 20 Kohlenstoffatome aufweisen.
5. Verfahren gemäß Anspruch 3, wobei  $R^1$  und  $R^2$  in der Formel (1) ein Fluoralkylrest oder miteinander verbunden sind, um einen Fluoralkylenrest zu bilden.
6. Verfahren gemäß einem der Ansprüche 1 bis 5, wobei das halogenierte Olefin mit der organischen, halogenhaltigen Verbindung der Reaktion als Gemisch davon unterworfen wird.
7. Verfahren gemäß Anspruch 6, wobei das Gemisch des halogenierten Olefins mit der organischen, halogenhaltigen Verbindung ein Reaktionsproduktgemisch, hergestellt durch Umsetzen mindestens einer Verbindung, ausgewählt aus perhalogenierten, konjugierten Dienen und perhalogenierten Olefinen, welche durch Substituieren aller Wasserstoffatome der konjugierten Diene mit von einem Fluoratom verschiedenen Halogenatomen hergestellt wurden, mit Fluorwasserstoff ist.
8. Verfahren gemäß einem der Ansprüche 1 bis 7, wobei die Menge des Alkalimetallfluorids im Bereich von 1 bis 3 Äquivalenten bezogen auf die Menge der gesamten, in der Summe des halogenierten Olefins und der organischen, halogenhaltigen Verbindung enthaltenen, von einem Fluoratom verschiedenen Halogenatome liegt.
9. Verfahren gemäß einem der Ansprüche 1 bis 8, wobei das Alkalimetallfluorid Lithium-, Natrium-, Kalium-, Cäsium- oder Rubidiumfluorid ist.
10. Verfahren gemäß einem der Ansprüche 1 bis 9, wobei die Reaktion in einem organischen Medium durchgeführt wird.



11. Verfahren gemäß Anspruch 10, wobei die Menge des organischen Mediums im Bereich von 100 bis 1.000 Gewichtsteilen bezogen auf 100 Gewichtsteile Alkalimetallfluorid liegt.

12. Verfahren gemäß Anspruch 10 oder Anspruch 11, wobei das organische Medium ein aprotisches, polares Lösungsmittel ist.

13. Verfahren gemäß Anspruch 12, wobei das aprotische, polare Lösungsmittel Dimethylformamid, Dimethylacetamid, N-Methylpyrrolidon, N,N-Dimethylimidazolidinon, Dimethylsulfoxid oder Sulfolan ist.

14. Verfahren gemäß einem der Ansprüche 1 bis 13, wobei die Reaktion durchgeführt wird, während das fluoridierte Olefin aus einem Reaktor entnommen wird, der am oberen Teil des Reaktors mit einer Rektifiziersäule ausgestattet ist.

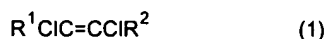
15. Verfahren gemäß einem der Ansprüche 1 bis 14, wobei die Reaktion in einem offenen System durchgeführt wird, während das halogenierte Olefin und die organische, halogenhaltige Verbindung in einem organischen Medium, in welchem das Alkalimetallfluorid dispergiert wurde, bereitgestellt werden und während das fluoridierte Olefin entnommen wird.

#### Revendications

1. Procédé de production d'une oléfine fluorée possédant une double liaison carbone-carbone, représentée par la formule suivante (3)

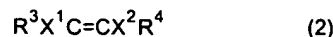


dans laquelle  $R^5$  et  $R^6$  représentent indépendamment un groupe alkyle ou fluoroalkyle ou un atome de fluor, ou  $R^5$  et  $R^6$  sont liés ensemble pour former un groupe alkylène ou fluoroalkylène, qui consiste à laisser réagir une oléfine halogénée, représentée par la formule générale suivante (1) :



dans laquelle  $R^1$  et  $R^2$  représentent indépendamment un groupe alkyle, un groupe fluoroalkyle ou un atome de fluor, ou  $R^1$  et  $R^2$  peuvent être liés ensemble pour former un groupe alkylène ou un groupe fluoroalkylène, avec un fluorure de métal alcalin, caractérisé en ce que ladite réaction de l'oléfine halogénée avec le fluorure de métal alcalin s'effectue en présence d'un composé halogéné organique

représenté par la formule générale suivante (2) :



dans laquelle  $X^1$  et  $X^2$  représentent un atome d'halogène, et  $R^3$  et  $R^4$  représentent indépendamment un groupe alkyle, un groupe halogénoalkyle ou un atome d'halogène, ou  $R^3$  et  $R^4$  sont liés ensemble pour former un groupe halogénoalkylène, et soit  $R^3$  soit  $R^4$  possède un atome d'halogène différent d'un atome de fluor ; ledit composé halogéné organique de formule (2) étant capable de réagir avec le fluorure de métal alcalin pour donner l'oléfine halogénée recherchée de formule (3).

2. Procédé selon la revendication 1, dans lequel la quantité du composé halogéné organique se situe dans l'intervalle allant de 1 à 200 parties en poids par rapport à 100 parties en poids de l'oléfine halogénée.

3. Procédé selon la revendication 1 ou 2, dans lequel l'oléfine halogénée possède de 2 à 30 atomes de carbone.

4. Procédé selon la revendication 3, dans lequel les groupes alkyle, fluoroalkyle, alkylène et fluoroalkylène pour  $R^1$  et  $R^2$  dans la formule (1) possèdent de 1 à 20 atomes de carbone.

5. Procédé selon la revendication 3, dans lequel  $R^1$  et  $R^2$  dans la formule (1) représentent un groupe fluoroalkyle ou sont liés ensemble pour former un groupe fluoroalkylène.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel l'oléfine halogénée est soumise à la réaction sous la forme d'un de ses mélanges avec le composé halogéné organique.

7. Procédé selon la revendication 6, dans lequel le mélange de l'oléfine halogénée avec le composé halogéné organique est un mélange du produit de réaction préparé en faisant réagir au moins un composé choisi parmi les diènes conjugués perhalogénés et les oléfines perhalogénées, qui ont été préparés en remplaçant la totalité des atomes d'hydrogène des diènes conjugués par des atomes d'halogène différents de l'atome de fluor, avec le fluorure d'hydrogène.

8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel la quantité de fluorure de métal alcalin se situe dans l'intervalle allant de 1 à 3 équivalents par rapport à la quantité de la totalité des atomes d'halogène autres qu'un atome de fluor con-

tenu dans la somme de l'oléfine halogénée et du composé halogéné organique.

9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel le fluorure de métal alcalin est le fluorure de lithium, le fluorure de sodium, le fluorure de potassium, le fluorure de césium ou le fluorure de rubidium. 5
10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel la réaction s'effectue dans un milieu organique. 10
11. Procédé selon la revendication 10, dans lequel la quantité du milieu organique se situe dans l'intervalle allant de 100 à 1000 parties en poids par rapport à 100 parties en poids du fluorure de métal alcalin. 15
12. Procédé selon la revendication 10 ou 11, dans lequel le milieu organique est un solvant polaire aprotique. 20
13. Procédé selon la revendication 12, dans lequel le solvant polaire aprotique est le diméthylformamide, le diméthylacétamide, la N-méthylpyrrolidone, la N, N-diméthylimidazolidinone, le diméthylsulfoxyde ou le sulfolane. 25
14. Procédé selon l'une quelconque des revendications 1 à 13, dans lequel la réaction s'effectue alors que l'oléfine fluorée est retirée d'un réacteur qui est muni d'une colonne de rectification à la partie supérieure du réacteur. 30
15. Procédé selon l'une quelconque des revendications 1 à 14, dans lequel la réaction s'effectue dans un système ouvert alors que l'oléfine halogénée et le composé halogéné organique sont amenés dans un milieu organique dans lequel le fluorure de métal alcalin a été dispersé, et tandis que l'oléfine fluorée est retirée. 35 40 45 50 55